

# Permutationally Invariant Polynomial Basis for Molecular Energy Surface Fitting via Monomial Symmetrization

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## Abstract

We describe a procedure to develop a fitting basis for molecular potential energy surfaces (PES) that is invariant with respect to permutation of like atoms. The method is based on a straightforward symmetrization of a primitive monomial basis and is illustrated for several classes of molecules. A numerically efficient method to evaluate the resulting expression for the PES is also described. The fitting basis is used to obtain a new PES for  $\text{H}_3\text{O}^+$  based on roughly 62 000 *ab initio* energies.

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# 1 Introduction

The representation of potential energy surfaces (PESs) that are fits to electronic energies is a long-standing goal of computational chemistry.<sup>1-3</sup> Progress to extend this goal beyond three and four-atom systems has been made recently by using a fitting basis that is invariant with respect to all permutations of like atoms.<sup>4</sup> (Also consult this paper for a review of other recent approaches to fitting PESs.) The approach makes use of powerful algorithms from computational invariant polynomial theory. The key feature of this method is to compute the *primary* and *secondary* invariants for a particular molecule permutation group. Once the primary and secondary invariants are computed, every invariant polynomial basis function can be uniquely factorized as the product of a secondary invariants with a polynomial of the primary invariants (typically this polynomial is just a product of some primary invariants when constructing the invariant basis functions). The computational efficiency of this representation comes from this factorization. Since every invariant polynomial can be written as the product of two invariant polynomials, hence in the real evaluation of the potential energy function, only  $N$  multiplications are need to evaluate all the  $N$  basis functions, once the necessary multiplication and additions are done to evaluate the primary and secondary invariants.

This method has been applied into a variety of molecules and molecular systems such as  $\text{CH}_5^+$ ,<sup>5-7</sup>  $\text{H}_5^+$ ,<sup>8,9</sup>  $\text{C}_2\text{H}_3$ ,<sup>10</sup>  $\text{H} + \text{CH}_4$ ,<sup>11-13</sup>  $\text{F} + \text{CH}_4$ ,<sup>14,15</sup> malonaldehyde ( $\text{CHOCH}_2\text{CHO}$ ),<sup>16</sup>  $\text{H}_3\text{O}^+$ ,<sup>17</sup>  $\text{OH} + \text{NO}_2$ ,<sup>18</sup>  $\text{HO}_2 + \text{NO}$ ,<sup>19</sup>  $\text{H}_5\text{O}_2^+$ ,<sup>20</sup> and water dimer  $(\text{H}_2\text{O})_2$ .<sup>21,22</sup> The large set of primary and secondary polynomial for as many as ten atom molecules was obtained with the commercial code MAGMA.<sup>23</sup> This large library of fitting bases is available at the iOpenShell web site.<sup>24</sup>

A much more straightforward approach to develop a permutationally invariant basis, termed monomial symmetrization was briefly and only schematically described by Huang *et al.*<sup>20</sup> The method was described in more detail in one of the author's Ph.D thesis<sup>25</sup> and recently reviewed and illustrated for several molecules.<sup>4</sup>

The monomial symmetrization approach (MSA) appears *prima facie* to be much less efficient than the invariant polynomial approach and so its presentation was mainly done as a pedagogi-

cal tool. In this paper we describe a method to make this straightforward fitting procedure quite efficient and thus potentially competitive with the computation invariant polynomial approach. Another key point of the paper is to show that the implementation of the approach is fairly straightforward and does not require access to the MAGMA code.

The paper is organized as follows. A brief review of the monomial symmetrization approach is presented in Section 2, followed by the algorithm to speed up the function evaluation process. The method is exemplified by an application for the  $\text{H}_3\text{O}^+$  molecule. In Section 3, numerical experiment results for this approach are compared with the computation invariant polynomial approach. A brief discussion including some possible new directions using this approach is given in Section 4. A summary and conclusions are given in Section 5.

## 2 Theoretical Background and Computational Details

### 2.1 Coordinate Representation of the Potential Energy Surface

The molecular potential energy surface, which we denote as  $V$ , should respect the key invariant properties of the physics. The well-known ones are overall translational and rotational invariance. A third one, that is obvious, but much less well known is invariance with respect to all permutations of like atoms. This invariance has been noted in the classic book by Murrell and co-workers<sup>1</sup> and is at the heart of the approach recently reviewed by Braams and Bowman.<sup>4</sup> As noted in that review and the primary sources cited there, the ideal choice of coordinates for  $V$  should enable these invariance properties to be “built in”. The full set of internuclear distances (of which there are  $\frac{n(n-1)}{2}$  for a system of  $n$  atoms) almost satisfy this property. That is these distances are invariant with respect to overall translation and rotation of the molecular system. They are not invariant with respect to permutation of like atoms; however, they are closed under these permutations and that is the property that has been exploited to make basis functions for the representation of  $V$  obey that invariance.

Before we show how this can be done using the MSA<sup>4,20,25</sup> we make two important remarks.

First, the full set of internuclear distances is known as a redundant set of coordinates since it is well known that only  $3n - 6$  internal degrees of freedom are needed to specify an  $n$  atom molecular configuration. Thus for  $n$  greater than four there are more internuclear distances than internal degrees of freedom and in that sense the choice is internuclear distances enlarges the space of variables for  $n > 4$ . Second, and independent of the value of  $n$ , internuclear distances are not a good choice of variables for a monomial or polynomial basis to represent  $V$ . This is because these distances become arbitrarily large when fragments form and thus  $V$  would diverge erroneously in these regions. Thus we and others use simple transformed variables that go to a constant in these regions. There are several choices for these variables that we have used and some of these choices will be given below and a specific choice is made when we consider an application to the  $\text{H}_3\text{O}^+$  PES. However, to investigate how these variables permute under permutations of like atoms it is sufficient to consider the set of internuclear distances and so we do that here.

To proceed we label the  $n$  atoms in a molecule as  $1, \dots, n$ , hence the  $\frac{n(n-1)}{2}$  internuclear distances in lexical order

$$(r_{1,2}, \dots, r_{1,n}, r_{2,3}, \dots, r_{2,n}, \dots, r_{n-1,n}).$$

Before proceeding we note that a choice of associated Morse variables that we have used extensively is  $y_{i,j} = \exp(-r_{i,j}/\lambda)$ . Also we introduce a shorthand notation for these distances (or Morse variables),  $x_l$ ,  $l = 1, n(n-1)/2$  where the  $x_l$  are ordered according to the lexical ordering of  $r_{i,j}$  ( $y_{i,j}$ ).

To proceed it is useful to consider a specific example of a tetraatomic molecule,  $\text{A}_4$ , and the six internuclear distances

$$(r_{1,2}, r_{1,3}, r_{1,4}, r_{2,3}, r_{2,4}, r_{3,4}).$$

and associated variables

$$(x_1, x_2, x_3, x_4, x_5, x_6).$$

The usual expression for  $V$  in terms of these variables is

$$V(x_1, x_2, x_3, x_4, x_5, x_6) = \sum_{a+b+c+d+e+f=0}^k C_{a,b,c,d,e,f} x_1^a x_2^b x_3^c x_4^d x_5^e x_6^f \quad (2.1)$$

where  $a, b, c, d, e$  and  $f$  are all non-negative integers, and  $k$  is a positive integer which sets the maximum as the sum of all the exponent. (The coefficients  $C_{a,b,c,d,e,f}$  would typically be determined by a standard linear least-squares fit to a data set of *ab initio* electronic energies.) Clearly this expression is not invariant with respect to permutations of like atoms. However, it is quite straightforward to modify the expression so that it is. This is done by symmetrizing the monomials, as discussed in detail elsewhere. This creates a sum of monomials with a single coefficient, which since it is determined by fitting we denote as  $D_{a,b,c,d,e,f}$ .<sup>4</sup> Consider an example permutation of the 4 atoms where the original atom order (1, 2, 3, 4) is permuted to (4, 2, 1, 3). The internuclear distances change from

$$(r_{1,2}, r_{1,3}, r_{1,4}, r_{2,3}, r_{2,4}, r_{3,4})$$

to

$$(r_{4,2}, r_{4,1}, r_{4,3}, r_{2,1}, r_{2,3}, r_{1,3}) \equiv (r_{2,4}, r_{1,4}, r_{3,4}, r_{1,2}, r_{2,3}, r_{1,3})$$

or in the “ $x$ ” notation

$$(x_1, x_2, x_3, x_4, x_5, x_6)$$

maps to

$$(x_5, x_3, x_6, x_1, x_4, x_2).$$

Thus the monomial  $x_1^a x_2^b x_3^c x_4^d x_5^e x_6^f$  maps to  $x_5^a x_3^b x_6^c x_1^d x_4^e x_2^f (\equiv x_1^d x_2^f x_3^b x_4^e x_5^a x_6^c)$ . To complete the symmetrization all permutations must be considered. We indicate the final result by

$$V = \sum_{a+b+c+d+e+f=0}^k D_{a,b,c,d,e,f} \mathcal{S}[x_1^a x_2^b x_3^c x_4^d x_5^e x_6^f], \quad (2.2)$$

where “ $\mathcal{S}$ ” is the operator that symmetrizes monomials. Examples of this were given for  $A_2B_2$

and  $A_3B$  molecules elsewhere.<sup>4</sup> This was done by explicitly enumerating all the permutations and showing how the internuclear distances permute. For a general molecule the total number of permutations is just the direct product of permutations of sets of like atoms. Thus for example for molecule  $A_nB_m$  the order of the direct-product symmetric group is  $n!m!$  and the full set of permutations of the sets of like atoms and how those map onto permutations of internuclear distances must be done. We note that if the resulting monomials are re-ordered in lexical form 1,2,3,etc. the effect of the mappings is equivalent to permuting the powers of the original “seed” monomial. We use this convention henceforth.

The generation of the permutation of internuclear distances (or equivalently the powers) has been automated with software we have written for any molecule<sup>26</sup> and Algorithm 1 summarizes the process.

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**Algorithm 1:** Monomial Symmetrization Approach

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```

Data:  $k$  ;                               // maximum total degree of monomials
Data:  $\mathcal{P}$  ;                           // permutation group
Result:  $B$  ;                               // invariant basis functions set
 $B \leftarrow \emptyset$ ;
 $m \leftarrow [0 \cdots 0]$ ;
while  $\text{deg}(m) \leq k$  do
     $\text{orb}(m) \leftarrow \{p_i \cdot m \mid p_i \in \mathcal{P}\}$ ;           //  $p_i$ : a permutation
     $B \leftarrow B \cup \text{orb}(m)$ ;
     $m \leftarrow m + 1$  ;                                     // get the next monomial
end

```

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## 2.2 Algorithm for Efficient Basis Evaluation

Though the potential energy function as shown in Equation 2.2 has the permutational invariant property, and we have the Algorithm 1 to generate the basis function set, the terms (the symmetrized sum of monomials) are costly to evaluate and so this representation is not nearly as efficient as the one based on *primary* and *secondary* invariants.<sup>4</sup> There clearly are strategies that can be used to speed up the evaluation of the symmetrized sum of monomials, which henceforth we denote as invariant polynomials.

Clearly if the invariant polynomials could be factored into lower order invariant polynomials that would achieve a great speed-up. To our knowledge this cannot be done easily (primary and secondary invariants essentially do this but the computation of primary and secondary invariants is difficult and complicated, as is the factorization). Here we describe and test a less ambitious factorization scheme, which is a binary factorization plus remainder method, where the remainder is another invariant polynomial, which may have already been computed. In order to describe this approach we introduce some new notation and nomenclature. As noted already an invariant polynomial (of some total degree) is the sum of all the monomials generated by acting all the possible permutations on a seed monomial. We denote this set of monomials as the orbit of the seed monomial  $m$ , and denote it as  $orb(m)$ , which could be represented as  $orb(m) = \{m^{p_i} | p_i \in \mathcal{P}\}$ . Hence Equation 2.2 can be simplified as

$$V(x_1, x_2, x_3, x_4, x_5, x_6) = \sum_{a+b+c+d+e+f=0}^k D[abcdef] \left( \sum_{\mathcal{P}} orb([abcdef]) \right), \quad (2.3)$$

where  $[abcdef]$  is a shorthand notation for a general monomial  $x_1^a x_2^b x_3^c x_4^d x_5^e x_6^f$ .

It is clear that if  $\sum_{\mathcal{P}} orb([abcdef])$  could be evaluated effectively, then the whole potential energy function could be computed effectively. One way to speed up this process is to evaluate or build these orbits recursively, i.e., express the “later” orbits as some simple expression from the “earlier” ones, where the terms “later” and “earlier” are yet to be defined as the ordering of monomials.

For monomials with different total degree, it is easy to order them according their total degree. For monomials with the same total degree, we order them according to the number of non-zero powers. For convenience, we order a monomial with more non-zero powers before another one with fewer non-zero elements but with same total degree, for instance,  $[010101] < [030000]$ . If two monomials have the same total degree and the same number of non-zero elements, then we order these monomials according to their lexicographical order, for example,  $[010101] < [101010]$ . This ordering scheme is made for later computational convenience. Similar to this ordering of monomi-

als, we can also order the polynomials or orbits, and here the polynomials are ordered according to the “largest” monomials (ordered in the last position according to the monomial ordering) in it. Note that for molecules with greater than four atoms the maximum total degree is typically much less than the number of internuclear distances there are no polynomials with where every  $x_i$  has a non-zero power.

To illustrate the approach consider the polynomial  $x_1^2 + x_2^2$ , which is invariant with respect to the permutation of  $x_1$  and  $x_2$ , and note that it cannot be simply decomposed as a product of two lower order polynomials. (It is in fact a primary invariant polynomial.) However, it can be given as a low order product with a remainder.

$$x_1^2 + x_2^2 = (x_1 + x_2)(x_1 + x_2) - x_1x_2 - x_1x_2.$$

As a result, if polynomial  $x_1 + x_2$  and  $x_1x_2$  are both in the invariant basis function sequence, and both appear “earlier” than  $x_1^2 + x_2^2$ , then  $x_1^2 + x_2^2$  could be very easily evaluated with one multiplication and two subtractions. To evaluate  $x_1^2 + x_2^2$  directly, we need two multiplications and one addition. Since multiplication is more expensive than addition or “subtraction” the decomposition should speed up the evaluation process. If such a decomposition can be found for a general invariant polynomial, the invariant basis function evaluation process will be greatly sped up.

Now the question comes to the existence and uniqueness of this kind of decomposition. Unfortunately, neither of these is guaranteed. For a successful decomposition, which we will denote as a “usable decomposition” it is required that the two polynomials that form the product be of lower degree, which of course they are, and also that the remainder polynomial come “before” the polynomial become decomposed. This is not always the case. Another issue for the decomposition is the uniqueness. Since there are various ways to factorize a high degree monomial as low degree ones, for example, for a monomial  $[012101]$ , it can be factorized as

$$[012101] = [010001] \cdot [002100]$$



or

$$[012101] = [011101] \cdot [001000]$$

or any other two monomials whose sum of exponents equal to the original exponents. Different factorizations of the monomials result in different remainder polynomials, and different factorization may or may not lead to a usable decomposition of a high degree polynomial.

One practical to approach to this factorization of polynomials is to list all the possible factorizations of the seed (it can be any monomial of the polynomial) of a high degree polynomial. Denoting the high degree polynomial as  $p_1$ , and one monomial in  $p_1$  as  $m_1$ , we have  $p_1 = orb(m_1)$ , and note that we do not distinguish the set of monomials as  $orb(m_1)$  and the polynomial which is the sum of all the monomials in this set. Suppose  $p_2$  is a polynomial arranged before  $p_1$  in the invariant polynomial basis sequence, then we can scan over all the monomials in  $p_2$ , if there is one monomial ( $m_2$ ) in  $p_2$  that is a factor of  $m_1$ , then we can factorize  $m_1$  as  $m_1 = m_2 m_3$ , and further find the orbit of  $m_3$  ( $orb(m_3)$ ) in the polynomial basis. Further suppose  $p_3 = orb(m_3)$ , then we can form the product  $p_2 p_3$ . The difference between  $p_2 p_3$  and  $p_1$  should be a sum of orbits of some other monomials (sum of some other invariant polynomials), the fewer the polynomials need to subtract the better. If it is not possible to find a usable decomposition, then we have to evaluate the polynomial by evaluating every monomials first. Every monomials within a polynomial that has no usable decomposition are pushed into a queue. The speed up for this process is determined partially by the size of the monomial queue. If most of the polynomials can be decomposed successfully, the size of the monomial queue is small and the efficiency of the approach is high. For monomials in the queue, the evaluation process for them could also be sped up by factorizing the later ones as the product of earlier ones.

In summary, all the possible monomials with total degree less than some threshold are enumerated and grouped into orbits by the action of permutations. The sum of such monomials in a orbit is an invariant polynomial. They are arranged according to the polynomial ordering scheme as defined above. Then the polynomials are decomposed into the product of two polynomials and possibly subtracting a small number of same-order polynomials if this is possible. Otherwise, the

polynomial is kept as the sum of monomials. A factorization step is performed for every monomial from the previous step, and evaluated as the product of two previous ones. In the follow section, an example will be given to show the process.

The algorithms just described above are summarized as the Algorithm 2, 3 and 4.

### 2.3 Example: Basis Functions for $\text{H}_3\text{O}^+$

$\text{H}_3\text{O}^+$  is an important molecule in chemistry, and it has three identical hydrogen atoms which make it a good example to illustrate the MSA process. Of course the results shown apply to any  $\text{A}_3\text{B}$  molecule.

The three H atoms are labeled as 1, 2, 3 and the O atom is labeled as 4. Table 1 shows all the permutation actions on  $\text{H}_3\text{O}^+$  and also on a general monomial  $[abcdef]$ . For the demonstration purpose,  $a, \dots, f$  are all different integers, in reality, some of them may be equal, consequently, the orbit of a monomial  $[abcdef]$  may has less than 6 monomials, and this is shown in Table 2.

Table 2 lists all the invariant polynomial basis for molecule  $\text{H}_3\text{O}^+$  up to degree 3. All those polynomials that have usable decomposition under the polynomial ordering scheme are indicated as a product of two other basis function less some other basis functions. As for those do not have usable decomposition, the decomposition is written as the sum of monomials.

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**Algorithm 2:** Trial and error decomposition algorithm for all the permutationally invariant basis functions

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```

Data:  $B$  ;                                // invariant basis functions set
Result:  $D$  ;                                // decomposition of  $b_i \in B$ 
Result:  $M$  ;                                // monomial set
 $B_P \leftarrow \emptyset$  ;                    // single term polynomial set
// populate the single term polynomial set
foreach  $b_i \in B$  do
    if  $|b_i| = 1$  then
         $B_P \leftarrow B_P \cup b_i$  ;
    end
end
// trying to decompose every basis function
 $M \leftarrow \emptyset$  ;
 $i_M \leftarrow 0$  ;                            // size index of  $M$ 
foreach  $b_i \in B$  do
    if  $b_i \in B_P$  then
        // deal with single term basis function
         $M \leftarrow M \cup b_i$  ;
         $i_M \leftarrow i_M + 1$  ;
         $D \leftarrow D \cup [i, 0, i_M]$  ;        // 0 indicates failed decomposition
    else
        // deal with multiple terms basis function
        if  $(\exists b_m, b_n, b_{l_1}, \dots \leq b_i) \vee (b_i = b_m \cdot b_n - b_{l_1} - \dots)$  then
            // the basis function has a usable decomposition
             $D \leftarrow D \cup [i, 1, m, n, l_1, \dots]$  ;    // 1 indicates successful
            decomposition
        else
            // the basis function has no usable decomposition
             $M \leftarrow M \cup \text{mono}(b_i)$  ;                // save the monomial set
             $D \leftarrow D \cup [i, 0, i_M + 1, \dots, i_M + |b_i|]$  ; // record the sum of monomials
             $i_M \leftarrow i_M + |b_i|$  ;
        end
    end
end
end

```

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**Algorithm 3:** Decomposition of a basis function (polynomial)  $b_i$ 

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**Data:**  $B, b_i \in B$ ; // invariant basis functions set, and one basis  
**Result:**  $b_i = b_m \cdot b_n - b_l \cdots$ ,  $(m, n, l, \cdots \leq i)$  or fail  
 $D \leftarrow \emptyset$ ; // usable decomposition set  
 $m_1 \leftarrow \text{seed}(b_i)$ ; //  $m_1 \in \text{mono}(b_i)$   
**foreach**  $b_j \in B \vee b_j < b_i$  **do**  
    **if**  $\exists m_2 \in \text{mono}(b_j) \vee m_1 = m_2 \cdot m_3$  **then**  
         $b_m \leftarrow b_j$ ;  
         $b_n \leftarrow \text{orb}(m_3)$ ;  
         $p \leftarrow b_m \times b_n - b_i$ ;  
        **if**  $(\exists b_{l_1}, \cdots \in B) \vee (b_{l_1}, \cdots < b_i) \vee (p = \sum_i b_{l_i})$  **then**  
             $D \leftarrow D \cup [i, m, n, l_1, \cdots]$ ;  
        **end**  
    **end**  
**end**  
**if**  $D = \emptyset$  **then**  
    **return** *fail*;  
**else**  
    **return**  $d \in D : |d| \leq |d_i|, \forall d_i \in D$ ; // return the simplest decomposition  
**end**

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**Algorithm 4:** Decomposition of Monomials

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**Data:**  $M$ ; // a monomial set  
**Result:**  $H$ ; // the decomposition of monomials  
 $H \leftarrow \emptyset$ ;  
**foreach**  $m \in M$  **do**  
    **if**  $(\exists m_i, m_j \in M) \vee (m_i, m_j < m) \vee (m = m_i \cdot m_j)$  **then**  
         $H \leftarrow H \cup [i, j]$ ;  
    **else**  
         $H \leftarrow H \cup m$ ;  
    **end**  
**end**

---

Table 1: The permutation of the  $\text{H}_3\text{O}^+$  molecule and its action on a general monomial [ abcdef ]

Permutation	Atom Labels	Internuclear Distance Vector	Permuted Monomial
$p_1$	1 2 3 4	$(x_1, x_2, x_3, x_4, x_5, x_6)$	[ abcdef ]
$p_2$	1 3 2 4	$(x_2, x_1, x_3, x_4, x_6, x_5)$	[ bacdfe ]
$p_3$	2 1 3 4	$(x_1, x_4, x_5, x_2, x_3, x_6)$	[ adebcf ]
$p_4$	2 3 1 4	$(x_4, x_1, x_5, x_2, x_6, x_3)$	[ daebfc ]
$p_5$	3 1 2 4	$(x_2, x_4, x_6, x_1, x_3, x_5)$	[ bdface ]
$p_6$	3 2 1 4	$(x_4, x_2, x_6, x_1, x_5, x_3)$	[ dbfaec ]

Table 2: invariant polynomials basis for molecule  $\text{H}_3\text{O}^+$  up to degree 3

ID	degree	invariant polynomial basis	Decomposition
$B_0$	0	[000000]	$M_0$
$B_1$	1	[000001] + [000010] + [001000]	$M_1 + M_2 + M_3$
$B_2$	1	[000100] + [010000] + [100000]	$M_4 + M_5 + M_6$
$B_3$	2	[000011] + [001001] + [001010]	$M_7 + M_8 + M_9$
$B_4$	2	[001100] + [010010] + [100001]	$M_{10} + M_{11} + M_{12}$
$B_5$	2	[000101] + [000110] + [010001] + [011000] + [100010] + [101000]	$B_1 \cdot B_2 - B_4$
$B_6$	2	[010100] + [100100] + [110000]	$M_{13} + M_{14} + M_{15}$
$B_7$	2	[000002] + [000020] + [002000]	$B_1 \cdot B_1 - B_3 - B_3$
$B_8$	2	[000200] + [020000] + [200000]	$B_2 \cdot B_2 - B_6 - B_6$
$B_9$	3	[001011]	$M_{16}$
$B_{10}$	3	[001101] + [001110] + [010011] + [011010] + [100011] + [101001]	$M_{17} + M_{18} + M_{19} + M_{20} + M_{21} + M_{22}$
$B_{11}$	3	[000111] + [011001] + [101010]	$B_2 \cdot B_3 - B_{10}$
$B_{12}$	3	[010110] + [011100] + [100101] + [101100] + [110001] + [110010]	$M_{23} + M_{24} + M_{25} + M_{26} + M_{27} + M_{28}$
$B_{13}$	3	[110100]	$M_{29}$
$B_{14}$	3	[010101] + [100110] + [111000]	$B_1 \cdot B_6 - B_{12}$
$B_{15}$	3	[000012] + [000021] + [001002] + [001020] + [002001] + [002010]	$B_1 \cdot B_3 - B_9 - B_9 - B_9$
$B_{16}$	3	[002100] + [010020] + [100002]	$B_1 \cdot B_4 - B_{10}$
$B_{17}$	3	[000102] + [000120] + [010002] + [012000] + [100020] + [102000]	$B_2 \cdot B_7 - B_{16}$
$B_{18}$	3	[001200] + [020010] + [200001]	$B_2 \cdot B_4 - B_{12}$
$B_{19}$	3	[000201] + [000210] + [020001] + [021000] + [200010] + [201000]	$B_1 \cdot B_8 - B_{18}$
$B_{20}$	3	[010200] + [020100] + [100200] + [120000] + [200100] + [210000]	$B_2 \cdot B_6 - B_{13} - B_{13} - B_{13}$
$B_{21}$	3	[000003] + [000030] + [003000]	$B_1 \cdot B_7 - B_{15}$
$B_{22}$	3	[000300] + [030000] + [300000]	$B_2 \cdot B_8 - B_{20}$

The factorization of all the monomials is shown in Table 3.

Table 3: Factorization of the monomials from those basis functions that do not have usable decomposition for  $\text{H}_3\text{O}^+$  molecule

ID	Monomial	factorization	ID	Monomial	factorization
$M_0$	[000000]	1	$M_{15}$	[110000]	$M_5 \cdot M_6$
$M_1$	[000001]	$x_6$	$M_{16}$	[001011]	$M_1 \cdot M_9$
$M_2$	[000010]	$x_5$	$M_{17}$	[001101]	$M_1 \cdot M_{10}$
$M_3$	[001000]	$x_3$	$M_{18}$	[001110]	$M_2 \cdot M_{10}$
$M_4$	[000100]	$x_4$	$M_{19}$	[010011]	$M_1 \cdot M_{11}$
$M_5$	[010000]	$x_2$	$M_{20}$	[011010]	$M_3 \cdot M_{11}$
$M_6$	[100000]	$x_1$	$M_{21}$	[100011]	$M_2 \cdot M_{12}$
$M_7$	[000011]	$M_1 \cdot M_2$	$M_{22}$	[101001]	$M_3 \cdot M_{12}$
$M_8$	[001001]	$M_1 \cdot M_3$	$M_{23}$	[010110]	$M_2 \cdot M_{13}$
$M_9$	[001010]	$M_2 \cdot M_3$	$M_{24}$	[011100]	$M_3 \cdot M_{13}$
$M_{10}$	[001100]	$M_3 \cdot M_4$	$M_{25}$	[100101]	$M_1 \cdot M_{14}$
$M_{11}$	[010010]	$M_2 \cdot M_5$	$M_{26}$	[101100]	$M_3 \cdot M_{14}$
$M_{12}$	[100001]	$M_1 \cdot M_6$	$M_{27}$	[110001]	$M_1 \cdot M_{15}$
$M_{13}$	[010100]	$M_4 \cdot M_5$	$M_{28}$	[110010]	$M_2 \cdot M_{15}$
$M_{14}$	[100100]	$M_4 \cdot M_6$	$M_{29}$	[110100]	$M_4 \cdot M_{15}$

As we can see from Table 2, quite a lot of the basis functions have usable decompositions, and can be expressed as the product of two lower degree basis functions and less some other basis functions at the same degree but come before the current invariant basis. As a result, the evaluation of those basis function cost one multiplication with some addition. For those monomials, almost all of them could be factorized as a product of two previous ones, this significantly reduced the monomial evaluation time especially when the total degree of monomial get higher and higher. All those monomials that can not be factorized are those single variable terms, and they are trivial to evaluate.

## 2.4 Applications to Other Molecules

Relevant information about the monomial and symmetrized monomial basis for a variety of molecules and total degree is given in Table 4. Columns three and four give the size of the monomial and symmetrized monomial (polynomial) basis for each example. The reduction in size for the polyno-

mial basis is large. However, it is not as large as the order of the corresponding symmetric group; this reduction factor is only approached as the total degree approaches infinity. For example for  $A_4$  the maximum possible reduction is 24 and as seen for degree 8 the actual reduction is 15.4. Next consider the number of polynomials and the percentage of the of all polynomials that have a usable decomposition shown in column 5 and 6. The percent ranges from almost 100 % to a low of 51.95 %. The number of remainder monomials to be evaluated and the number that can be factored are given next. Finally, an "Efficiency" column is included which contains two values. The ratio of total monomials to total polynomials is given in parentheses and the first number is the ratio of monomials to the sum of usable decomposition plus monomials left.

Table 4: Invariant Polynomial Basis Function Decomposition Information

Molecule	Max Deg	Tot Mono.	Tot Poly.	Usable Decomp.	Usable Decomp. %	Mono Left	Mono Fact	Efficiency
$A_3$	6	84	23	19	82.61 %	8	4	3.11 (3.65)
$A_3$	8	165	41	37	90.24 %	8	4	3.67 (4.02)
$A_2B$	6	84	50	46	92.00 %	5	1	1.65 (1.68)
$A_2B$	8	165	95	91	95.79 %	5	1	1.72 (1.74)
$A_4$	6	924	72	60	83.33 %	88	81	6.24 (12.83)
$A_4$	8	3003	195	182	93.33 %	112	105	10.21 (15.40)
$A_3B$	6	924	196	185	94.39 %	33	26	4.24 (4.71)
$A_3B$	8	3003	590	579	98.14 %	33	26	4.91 (5.09)
$A_2B_2$	6	924	291	282	96.91 %	18	11	3.08 (3.18)
$A_2B_2$	8	3003	882	873	98.98 %	18	11	3.37 (3.40)
$A_2BC$	6	924	502	494	98.41 %	11	4	1.83 (1.84)
$A_2BC$	8	3003	1589	1581	99.50 %	11	4	1.89 (1.89)
$A_5$	6	8008	140	94	67.14 %	2368	2357	3.25 (57.20)
$A_5$	8	43758	580	443	76.38 %	10158	10147	4.13 (75.44)
$A_4B$	6	8008	495	437	88.28 %	807	796	6.44 (16.18)
$A_4B$	8	43758	2327	2216	95.23 %	1953	1942	10.50 (18.80)
$A_3B_2$	6	8008	889	838	94.26 %	390	367	6.52 (9.01)
$A_3B_2$	8	43758	4343	4249	97.84 %	876	853	8.54 (10.08)
$A_3BC$	6	8008	1603	1565	97.63 %	161	150	4.64 (5.00)
$A_3BC$	8	43758	8163	8121	99.49 %	185	174	5.27 (5.36)
$A_2B_2C$	6	8008	2304	2278	98.87 %	72	61	3.41 (3.48)
$A_2B_2C$	8	43758	11910	11884	99.78 %	72	61	3.66 (3.67)
$A_2BCD$	6	8008	4264	4249	99.65 %	22	11	1.87 (1.88)
$A_2BCD$	8	43758	22734	22719	99.93 %	22	11	1.92 (1.92)
$A_5B_2$	4	12650	218	148	67.89 %	4997	4975	2.46 (58.03)
$A_5B_2$	6	296010	2651	2080	78.46 %	78066	77924	3.69 (111.66)
$A_6B_3$	3	9139	77	40	51.95 %	5485	5448	1.65 (118.69)
$A_6B_3$	4	91390	327	208	63.61 %	47533	47496	1.91 (279.48)



Perusal of this table leads to the conclusion that the current factorization method works better for molecules with 2 or 3 identical atoms than for molecules with more identical atoms. On the other hand the size of polynomial basis decreases by a larger factor for such molecules (obviously since the order of the symmetric group increases).

The lack of usable decomposition for all (invariant) polynomials in the present algorithm comes from the polynomial ordering scheme. It is not difficult to show that any high degree invariant polynomial constructed using monomial symmetrization approach, can be represented as the product of two low degree polynomials and a remainder invariant polynomial of the same degree. If the polynomial ordering scheme can ensure that polynomials need to be subtracted are always come before the target polynomial, then the inefficiency factor could be removed and we can claim that the monomial symmetrization approach is almost as fast as the computation invariant theory based approach. However, this ordering scheme is difficult to construct. A simple example may show the difficulty. Suppose that  $x_1 + x_2$ ,  $x_1^2 + x_2^2$  and  $x_1x_2$  are invariant polynomials with respect to the permutation of  $x_1$  and  $x_2$ . Both  $x_1^2 + x_2^2$  and  $x_1x_2$  are of degree 2, and  $x_1 + x_2$  is of degree 1, which is always come before the other two polynomials.  $x_1^2 + x_2^2$  could be decomposed as

$$x_1^2 + x_2^2 = (x_1 + x_2) \cdot (x_1 + x_2) - x_1x_2 - x_1x_2 \quad (2.4)$$

and  $x_1x_2$  could be decomposed at

$$x_1x_2 = (x_1 + x_2) \cdot (x_1 + x_2) - (x_1^2 + x_2^2) - x_1x_2. \quad (2.5)$$

It is easy to rearrange Equation 2.5 as

$$2x_1x_2 = (x_1 + x_2) \cdot (x_1 + x_2) - (x_1^2 + x_2^2). \quad (2.6)$$

As can be seen, no matter the polynomial ordering scheme is (whether  $x_1x_2$  comes before  $x_1^2 + x_2^2$  or after it), there is always one useless decomposition. Unfortunately, one of  $x_1x_2$  and  $x_1^2 + x_2^2$  must

be evaluated explicitly. This coincide with the primary invariants.

In another case, suppose that we have invariants

$$\begin{aligned} A &= x_1^4 + x_2^4 \\ B &= x_1^2 x_2^2 \\ C &= x_1 x_2^3 + x_1^3 x_2, \end{aligned} \tag{2.7}$$

and they could be decomposed as

$$\begin{aligned} A &= (x_1^2 + x_2^2) \cdot (x_1^2 + x_2^2) - (x_1^2 x_2^2 + x_1^2 x_2^2) \\ B &= (x_1 x_2^2 + x_1^2 x_2) \cdot (x_1 + x_2) - (x_1 x_2^3 + x_1^3 x_2) - x_1^2 x_2^2 \\ C &= (x_1 + x_2) \cdot (x_1^3 + x_2^3) - (x_1^4 + x_2^4). \end{aligned} \tag{2.8}$$

$x_1 + x_2$ ,  $x_1^2 + x_2^2$ ,  $x_1^3 + x_2^3$  and  $x_1 x_2^2 + x_1^2 x_2$  are at lower degree comparing to  $A$ ,  $B$  and  $C$ , hence their values are supposed to be calculated. Consequently, the decomposition can be simplified as

$$\begin{aligned} A &= \alpha - 2B \\ B &= \beta - C - B \\ C &= \gamma - A, \end{aligned} \tag{2.9}$$

where

$$\begin{aligned} \alpha &= (x_1^2 + x_2^2) \cdot (x_1^2 + x_2^2) \\ \beta &= (x_1 x_2^2 + x_1^2 x_2) \cdot (x_1 + x_2) \\ \gamma &= (x_1 + x_2) \cdot (x_1^3 + x_2^3), \end{aligned} \tag{2.10}$$

and they can be regarded as constant.

It is obvious that  $A$ ,  $B$  and  $C$  are intertwined, and some of them must be evaluated by brute force. However, Equation 2.9 could be regarded as a linear system as

$$\begin{bmatrix} 1 & 2 & 0 \\ 0 & 2 & 1 \\ 1 & 0 & 1 \end{bmatrix} \cdot \begin{bmatrix} A \\ B \\ C \end{bmatrix} = \begin{bmatrix} \alpha \\ \beta \\ \gamma \end{bmatrix} \quad (2.11)$$

which can be solved easily as

$$\begin{aligned} A &= \frac{1}{2}\alpha - \frac{1}{2}\beta + \frac{1}{2}\gamma \\ B &= \frac{1}{4}\alpha + \frac{1}{4}\beta - \frac{1}{4}\gamma \\ C &= -\frac{1}{2}\alpha + \frac{1}{2}\beta + \frac{1}{2}\gamma. \end{aligned} \quad (2.12)$$

This indicates that it is possible to further decouple intertwined polynomials, and obtain their usable decomposition simultaneously by solving a linear system. Solving the linear system is an extra cost for the decomposition, but it is an one time cost, and it will not be inherited in the future polynomial evaluation process. As a result, we can further speed up the polynomial evaluation process. We plan to investigate an implementation of this algorithm in the future.

### 3 Application to a Potential Surface for $\text{H}_3\text{O}^+$

The methods described in the previous section to automate the symmetrization of the monomial basis and to evaluate the subsequent terms by means of the decomposition procedure are applied to the potential energy surface of  $\text{H}_3\text{O}^+$ . An unpublished PES for this cation was obtained using the invariant polynomial approach previously<sup>25</sup> and this serves as the “benchmark” PES both in terms of precision and speed of evaluations. The precision and speed of evaluation of the monomial symmetrization approach will be tested against this benchmark.

$\text{H}_3\text{O}^+$  potential energy surface is a well studied surface.<sup>17,27,28</sup> Previously, the invariant poly-

nomial basis functions were used for the fit and these were constructed based on computational invariant theory. Here we directly compare these two methods (both implemented in C++). The internuclear distances  $x$  are replaced by the variables  $1.0 - \exp(-0.2x)^2$  as usual.<sup>4</sup> 61604  $\text{H}_3\text{O}^+$  configurations were gathered by low-level direct molecular dynamics and further the energies were evaluated based on CCSD(T) method with aug-cc-pVTZ basis. The energy range for these configurations is about  $29674 \text{ cm}^{-1}$  (84.84 kcal/mol). The maximum total degree for the polynomial basis is set to be 6. This is the same total degree used for the invariant polynomial fit. Since both approach have the same number of basis functions, the number of coefficients is also the same. Note that the coefficients values are different since the basis functions from two approach differ. The coefficients for both fits were obtained with standard least-squares codes. The final root mean square error for both fitting approaches are  $29.03 \text{ cm}^{-1}$ , with the maximum absolute residual value deviation at  $0.16 \text{ cm}^{-1}$ . As expected, there is almost no difference is observed for the accuracy of these two approach.

After obtaining the coefficients, we evaluated the energies for the molecule configurations in the original data set used for fitting three times which results 184812 potential function calls in total. The computational invariant theory approach took 8.77 seconds, and the modified monomial symmetrization approach took 9.50 seconds. It is about 8% less efficiency for the monomial symmetrization approach which are almost negligibly. Comparing the details of these two approaches, it is not difficulty to notice and the slightly more time is consumed in evaluating and summing the monomials from those polynomial basis function that can not be effectively decomposed. For  $\text{H}_3\text{O}^+$  molecule, the number of monomials does not change when the maximum total degree of polynomial basis function get higher and higher. As a result, the timing difference would be virtually the same.

## 4 Discussion

Perhaps the most striking practical effect of symmetrizing the monomial expression for the potential, Equation 2.1 is the very large reduction in the number of terms and hence unknown linear coefficients to be determined. This was illustrated in Table 4 where the number of monomials in the unsymmetrized expression for  $V$  is compared to the number of symmetrized polynomials. The ratio of these two numbers approaches the order of the symmetric group in the limit of infinitely many terms in both expressions; however, as seen even for modest total orders the reduction can be very big. Practically this has allowed us to consider molecules with up to 9 atoms and to deal with a relatively small linear algebra least-squares minimization. This very practical advantage is realized by using the full permutation group of a molecule.

This practical advantage in exploiting the full permutational symmetry also holds for molecular complexes. For example consider the water dimer and trimer, where the order of the symmetric group is  $4!2! = 48$  and  $6!3! = 4320$ , respectively. Potential energy surfaces for both the water dimer and trimer, using the full permutational symmetry have been reported.<sup>16,29</sup> However, physically one knows that for temperatures or total energies of interest most of these permutations are infeasible, that is they must surmount high potential barriers to be realized. Thus it would seem that using the full symmetric group, while greatly reducing the number of terms in  $V$ , is also physically irrelevant. Ideally one would like a representation that both greatly reduces the number of terms in  $V$  and only describes the feasible permutations. (In the case of water clusters this would be the permutations of the H atoms associated with each monomer unit.) If one is going to continue to use all the internuclear distances (probably with a standard many-body representation of the potential) then it seems clear that the one will have to restrict the range of powers of some of the internuclear distances. The presumably would be the monomer internuclear distances which undergo small amplitude motion. In fact a rather primitive version of this type of restriction was used in a monomial representation of the global potential of  $\text{H}_2\text{CO}$  for the CO internuclear distance.<sup>30</sup> Further work along these lines is planned.

Also, as the observant reader has noted the use of the Morse-type variables introduces a non-

linear range parameter. Generally we have used a single range parameter, typically 2-3 Bohr, for all variables. In principle this parameter could be optimized and also made specific for a given set of internuclear distances, e.g., all OH, HH, and OO distances. Doing so would turn the straightforward linear-least squares optimization into a combination of linear and non-linear optimizations. This may be worth considering; however, with a substantial increase in numerical complexity.

Finally we note that the library of primary and secondary invariant polynomials referred to in the paper does not include analytical expressions for partial derivatives. This may be done in the future; however, it will involve considerable symbolic computation. It is clear that using the monomial symmetrization described here this task is made much easier for the user. We plan to do this in the near future.

## 5 Conclusions

We have presented a straightforward monomial symmetrization scheme for the representation of a multidimensional potential energy surface. We have proposed one scheme for efficient evaluation of the results terms in the representation and have illustrated the approach by fitting roughly 62,000 electronic energies for  $\text{H}_3\text{O}^+$ . Some comments for future directions were also made.

The codes described herein can be obtained by contacting either author.

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## References

- (1) Murrell, J. N. *Molecular potential energy functions*; J. Wiley: Chichester [West Sussex] ; New York, 1984.
- (2) Schatz, G. C. *Rev. Mod. Phys.* **1989**, *61*, 669–688.
- (3) Hollebeek, T.; Ho, T. S.; Rabitz, H. *Annu. Rev. Phys. Chem.* **1999**, *50*, 537–570.
- (4) Braams, B. J.; Bowman, J. M. *Int. Rev. Phys. Chem.* **2009**, in press.
- (5) Jin, Z.; Braams, B.; Bowman, J. *J. Phys. Chem. A* **2006**, *110*, 1569–1574.
- (6) Christoffel, K.; Jin, Z.; Braams, B.; Bowman, J. *J. Phys. Chem. A* **2007**, *111*, 6658–6664.
- (7) Mann, J.; Xie, Z.; Savee, J.; Braams, B.; Bowman, J.; Continetti, R. *J. Am. Chem. Soc.* **2008**, *130*, 3730.
- (8) Xie, Z.; Braams, B.; Bowman, J. *J. Chem. Phys.* **2005**, *122*, 224307.
- (9) Acioli, P.; Xie, Z.; Braams, B.; Bowman, J. *J. Chem. Phys.* **2008**, *128*, 104318.
- (10) Park, W.; Park, J.; Park, S.; Braams, B.; Chen, C.; Bowman, J. *J. Chem. Phys.* **2006**, *125*, 081101.
- (11) Zhang, X.; Braams, B.; Bowman, J. *J. Chem. Phys.* **2006**, *124*, 021104.
- (12) Xie, Z.; Bowman, J.; Zhang, X. *J. Chem. Phys.* **2006**, *125*, 133120.
- (13) Xie, Z.; Bowman, J. *Chem. Phys. Lett.* **2006**, *429*, 355–359.
- (14) Czako, G.; Braams, B.; Bowman, J. *J. Phys. Chem. A* **2008**, *112*, 7466–7472.
- (15) Czako, G.; Shepler, B.; Braams, B.; Bowman, J. *J. Chem. Phys.* **2009**, *130*, 084301.
- (16) Wang, Y.; Braams, B.; Bowman, J.; Carter, S.; Tew, D. *J. Chem. Phys.* **2008**, *128*, 224314.
- (17) Mann, J.; Xie, Z.; Savee, J.; Bowman, J.; Continetti, R. *J. Chem. Phys.* **2009**, *130*, 041102.

- (18) Chen, C.; Shepler, B.; Braams, B.; Bowman, J. *J. Chem. Phys.* **2007**, *127*, 104310.
- (19) Chen, C.; Shepler, B.; Braams, B.; Bowman, J. *Phys. Chem. Chem. Phys.* **2009**, *11*, 4722–4727.
- (20) Huang, X.; Braams, B.; Bowman, J. *J. Chem. Phys.* **2005**, *122*, 044308.
- (21) Huang, X.; Braams, B.; Bowman, J. *J. Phys. Chem. A* **2006**, *110*, 445–451.
- (22) Shank, A.; Wang, Y.; Kaledin, A.; Braams, B.; Bowman, J. *J. Chem. Phys.* **2009**, *130*, 144314.
- (23) Bosma, W.; Cannon, J.; Playoust, C. *J. Symbolic Comput.* **1997**, *24*, 235–265.
- (24) *iOpenShell*, <http://iopenshell.usc.edu/>.
- (25) Xie, Z. Ph.D. thesis, Emory University, 2008.
- (26) *MSA Code URL*, <http://www.mcs.anl.gov/~zhenxie/codes/msa.tgz>.
- (27) Huang, X.; Carter, S.; Bowman, J. *J. Chem. Phys.* **2003**, *118*, 5431–5441.
- (28) Rajamaki, T.; Miani, A.; Halonen, L. *J. Chem. Phys.* **2003**, *118*, 10929–10938.
- (29) Huang, X.; Braams, B.; Bowman, J.; Kelly, R.; Tennyson, J.; Groenenboom, G.; der avoird, A. V. *J. Chem. Phys.* **2008**, *128*, 034312.
- (30) Zhang, X. B.; Zou, S. L.; Harding, L. B.; Bowman, J. M. *J. Phys. Chem. A* **2004**, *108*, 8980–8986.